Activation of Molecular Oxygen by a Metal Complex. The Formation and Structure of the Anion $[Ph_3POFe(S_2C_2\{CF_3\}_2)_2]^-$

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Summary Triphenylphosphine reacts with $(Bu_4N)_2[Fe_2(S_2C_2\{CF_3\}_2)_4]$ in the presence of molecular oxygen to form a triphenylphosphine oxide adduct, $(Bu_4N)[Ph_3POFe(S_2C_2\{CF_3\}_2)_2]$, which had been previously formulated as a phosphine complex.

FURTHER studies on the crystalline complex originally described[1] as "$(Bu_4N)[Ph_3PFe(S_2C_2\{CF_3\}_2)_2]$" indicate that the complex is actually the triphenylphosphine oxide adduct, $(Bu_4N)[Ph_3POFe(S_2C_2\{CF_3\}_2)_2]$. The complex may be prepared by the original route, by slow evaporation of an Me_2CO–PhMe or CH_2Cl_2–PhMe solution of $(Bu_4N)_2[Fe_2(S_2C_2\{CF_3\}_2)_4]$ and triphenylphosphine, or directly from triphenylphosphine oxide and $[Fe_2(S_2C_2\{CF_3\}_2)_4]^{2-}$. Since the preparation from triphenylphosphine can be carried out in a system in which the only source of oxygen is the atmosphere, it appears that this reaction involves another case[2] of activation of molecular oxygen by a metal complex. Additional studies of the mechanism of this reaction are in progress. Attempts to verify the presence of the P–O unit in the complex by i.r. have been thwarted by the presence of several, strong, C–F stretching modes in the region, 1200—1100 cm^{-1}, where the P–O stretch should occur. However, the constitution of this complex has been ascertained by X-ray methods.

Crystal Data. The dark red substance crystallizes in the space group $P2_1/c$ with cell constants $a = 14{\cdot}855$ (5), $b = 15{\cdot}363$ (5), $c = 21{\cdot}628$ (9) Å and $\beta = 91{\cdot}82°$ (8), $V = 4933{\cdot}6$ (Å)^3; $D_m = 1{\cdot}37$; $D_c = 1{\cdot}39$ g.cm^{-3}, $Z = 4$. The data were collected in a four-circle Picker diffractometer equipped with a graphite monochromator and controlled by the Brookhaven Multiple Spectrometer System. Two forms of the asymmetric set of data were collected using Mo-K_α radiation. One form of the data was corrected for Lorentz-polarization effects and used for the solution of the structure. This procedure yielded 1568 significant reflections. The structure was solved by standard Patterson methods and initial phases were obtained from the positions of the iron and the four sulphur atoms. When the approximate co-ordinates of the non-hydrogen atoms of the cation and of the $Fe(S_2C_2\{CF_3\}_2)_2$ portion of the anion were obtained, the scale and overall temperature factor plus the positional parameters of the atoms were refined and a difference map computed. This map showed the presence of the phosphorus atom, two complete phenyl rings, and four carbon atoms of the third phenyl ring, all further removed than expected for a PPh_3-group bonded directly to the Fe atom. The difference map also revealed the presence of an atom between the iron and the phosphorus which was assumed to be an oxygen, and so refined (*vide supra*). Two cycles of refinement with all the atoms vibrating isotropically gave an R_F index of 0·16.

The stereochemical configuration of the anion is shown in the Figure. Some interatomic distances are given in the Table. In order to illustrate the stereochemical effect of injecting an extra electron into the diamagnetic compound, $[Ph_3AsFe(S_2C_2\{CF_3\}_2)_2]$,[1] the Table also includes pertinent interatomic distances from the neutral species.[3] As in the case of the porphins,[4] a noticeable change takes place in the metal–ligand bond lengths and in the displacement of the metal atom from the basal plane, the displacement being less for lower-spin species. In the neutral species, the Fe–S bonds are shorter than those in the anion; likewise, the height of the metal above the plane of the four basal sulphur ligands increases from 0·23 Å to 0·43 Å. The Fe–O–P unit is clearly bent (see Figure), the angle at the oxygen being 169°. Both linear[5a] and bent[5b] co-ordination by phosphine oxides have been reported. Anisotropic refinement of the Fe,4S, P, O, and 12F atoms while constraining the remaining atoms to isotropic thermal motion yields discrepancy indices of $R_1 = 0{\cdot}086$ and $R_2 = 0{\cdot}087$.

TABLE

	$Ph_3AsFe(S_2C_2\{CF_3\}_2)_2$	$[Ph_3POFe(S_2C_2\{CF_3\}_2)_2]^-$
Fe–S(1)	2·149*	2·225
Fe–S(2)	2·146	2·199
Fe–S(3)	2·154	2·239
Fe–S(4)	2·145	2·231
Fe–As	2·325	—
Fe–O	—	1·957
Δ(Fe)†	0·232	0·434
S(1) ··· S(2)‡ ..	3·021	3·096
S(3) ··· S(4)	3·023	3·077
S(1) ··· S(4)	2·952	3·026
S(2) ··· S(3)	3·087	3·139

* Estimated standard deviations on bond lengths at this stage of refinement are, for the anion Fe–S = 0·015 Å, S–S = 0·020 Å; for the neutral compound Fe–S = 0·003 Å, S–S = 0·005 Å.

† Δ = Displacement of the Fe from the mean plane of the four S-atoms.

‡ Non-bonded distances.

The anion $[Ph_3PFe(S_2C_2\{CF_3\}_2)_2]^-$ has not been isolated but evidence for its presence in solution exists. The electronic spectra of $[Fe_2(S_2C_2\{CF_3\}_2)_4]^{2-}$ in dichloromethane solution in the presence of varying quantities of triphenylphosphine contain five isosbestic points in the region 700—350 nm, indicating the presence of two complexes. Over short periods of time the spectrum of $[Ph_3PFe(S_2C_2\{CF_3\}_2)_2]^-$ so obtained is not affected by the presence of molecular oxygen, and this spectrum is significantly different from the spectrum obtained from the solid phosphine oxide adduct. The phosphine adduct in the presence of an excess of phosphine is oxidized polarographically at +0·32 v to the corresponding neutral complex as previously described.[1] Under similar conditions, the phosphine oxide adduct undergoes polarographic oxidation at about 0·7 v but the process may be more complex than a one-electron oxidation. None of the other five-co-ordinate, bis-dithiolene adducts reported in ref. 1 appear to involve an oxide of the type R_3EO (E = P, As, Sb).

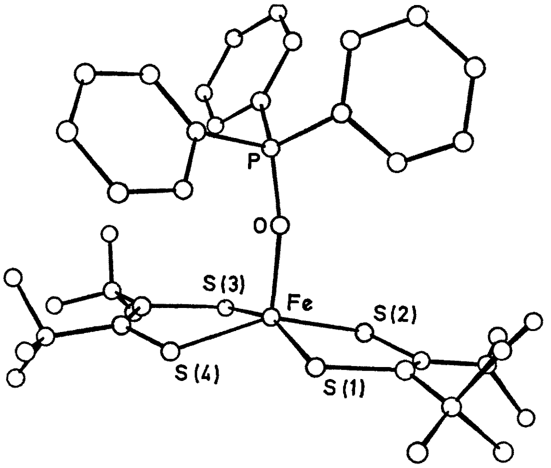

FIGURE. *Stereochemical configuration of the anion in* $[Bu_4N][Ph_3POFe(C_2S_2\{CF_3\}_2)_2]$. *For the sake of illustrative neatness the thermal motions of all atoms were arbitrarily made equal and isotropic.*

The magnetic susceptibility of $(Bu_4N)[Ph_3POFe(S_2C_2\{CF_3\}_2)_2]$ at 298°K is 4·00 BM, which indicates a quartet ground state. It now appears that five-co-ordinate complexes of the type $[LFe(S–S)_2]^-$, where (S–S) represents a dithiolene ligand, exhibit quartet ground states when L co-ordinates through a "hard" donor such as N or O, but have doublet ground states when L co-ordinates through a "soft" donor such as P, As, or C.[6]

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